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Sequential Fullerenylation of Bis-malonates – Efficient Access to Oligoclusters with Different Fullerene Building Blocks

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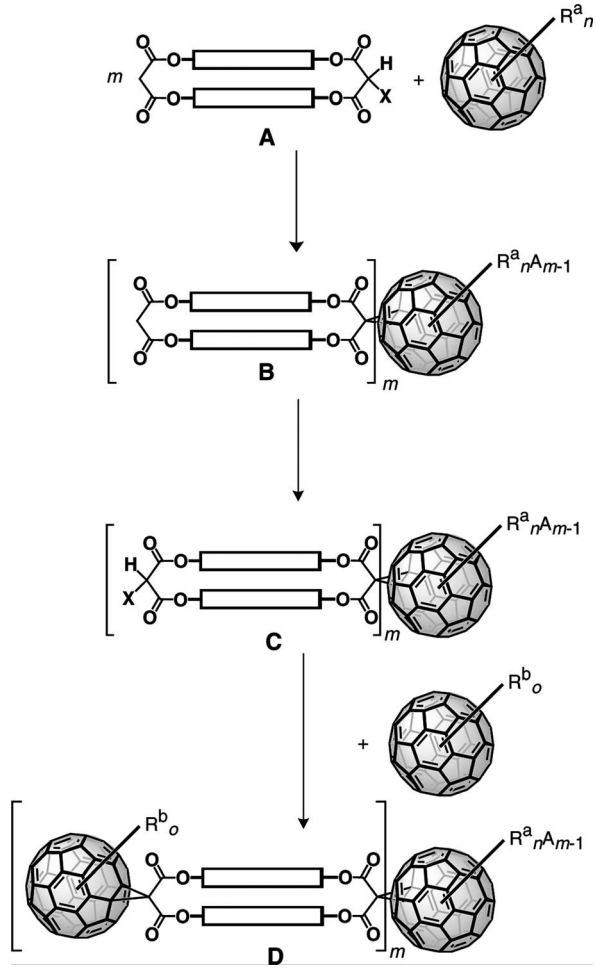
A method for the sequential fullerenylation of bis-malonates with parent C_{60} and C_{2v}-symmetric pentakis-adducts is reported. This approach relies on the finding that (a) chloromalonates can be used for the nucleophilic cyclopropanation of [6,6] double bonds of C_{60}, and (b) chloromalonates, in contrast to bromomalonates, do not undergo base-catalyzed halogen exchange reactions. For the proof of concept, we synthesized a heptafullerene by using a divergent approach based on a fullerene hexakis-adduct with six bis-malonate addends in octahedral positions, each of which is suitable for an additional cyclopropanation of a fullerene building block.

Introduction

The nucleophilic cyclopropanation of fullerenes was originally described by Bingel and belongs to the most important transformations in fullerene chemistry.[1] In such a reaction, 1,3-dicarbonyl compounds, in most cases malonates, are first transformed into the corresponding monobromides or monoiodides and then added to a [6,6] double bond of the fullerene, promoted by deprotonation of the acidic H atom located at C-2. Monohalides can be either used directly or prepared in situ.[2–4] For the highly regioselective oligoaddition of malonates to C_{60} to form bis-, tris-, and tetrakismalonates with a stereochemically defined addition pattern, we have developed the addition chemistry of cyclo-[*n*]-malonates, in which several malonates (e.g., 2–4) are linked together with alkano bridges to form a macrocycle.[5] On the other hand, these cyclo-[*n*]-malonates offer the opportunity to successively bind several fullerene building blocks of different natures, for example, with variations of the exohedral functionalities, the degree of addition, and the addition pattern. In this manner, a modular system of highly functional macromolecules with tunable properties would become available. Nierengarten and co-workers undertook different approaches for the controlled construction of multifullerene dendrimers,[6] which relied on asymmetric coupling reactions of fullerene adducts and led to further reactive sites in the linker. However, the attempt to build unsymmetric structures by using the same reaction on either end of the linker, as we want to, requires a selective and controlled addition of one malonate followed by the other to the corresponding fullerene building blocks. The



Scheme 1.Sequential fullerenylation of cyclo-[2]-malonates with two different fullerene adducts.

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sequential functionalization of macrocyclic bis-malonates with two different fullerene building blocks is exemplified in Scheme 1.

The obvious way to realize such an approach would be to monobrominate the bis-malonate on one side, fullerenylate it by letting only the brominated side react, monobrominate the second malonate site, and finally perform the remaining fullerenylation with another building block. However, in preliminary experiments, we realized that a controlled sequential addition cannot be accomplished, presumably because of scrambling of the Br atom between both malonate sites. Recently, we have also shown that, very unexpectedly, bis(bromo)malonates are also able to cyclopropanate fullerenes and we have provided an explanation for this observation.[7] These developments and the challenge of gaining control over the step-by-step fullerenylation of oligomalonates require a) methods that increase the selectivity of the sequential addition by eliminating scrambling reactions and b) further investigations of the mechanisms of cylopropanation chemistry. Moreover, systematic studies that reveal the role of X in the malonates depicted in Scheme 1 are required.

In this paper, we report on the successful avoidance of halogen scrambling reactions by introducing the use of chloromalonates as addends, and we exemplify highly selective and sequential fullerenylation of bis-malonates with the divergent synthesis of the heptafullerene **1** (Figure 1).

Results and Discussion

To systematically address the question of Br scrambling mentioned above, we treated diethyl 2-bromomalonate (**2**) in the presence of cyclo-[2]-octylmalonate (**3**) with diazabicycloundecene (DBU) in the absence of C_{60}. These are typical conditions for the cyclopropanation of fullerenes (Scheme 2).[1,2]

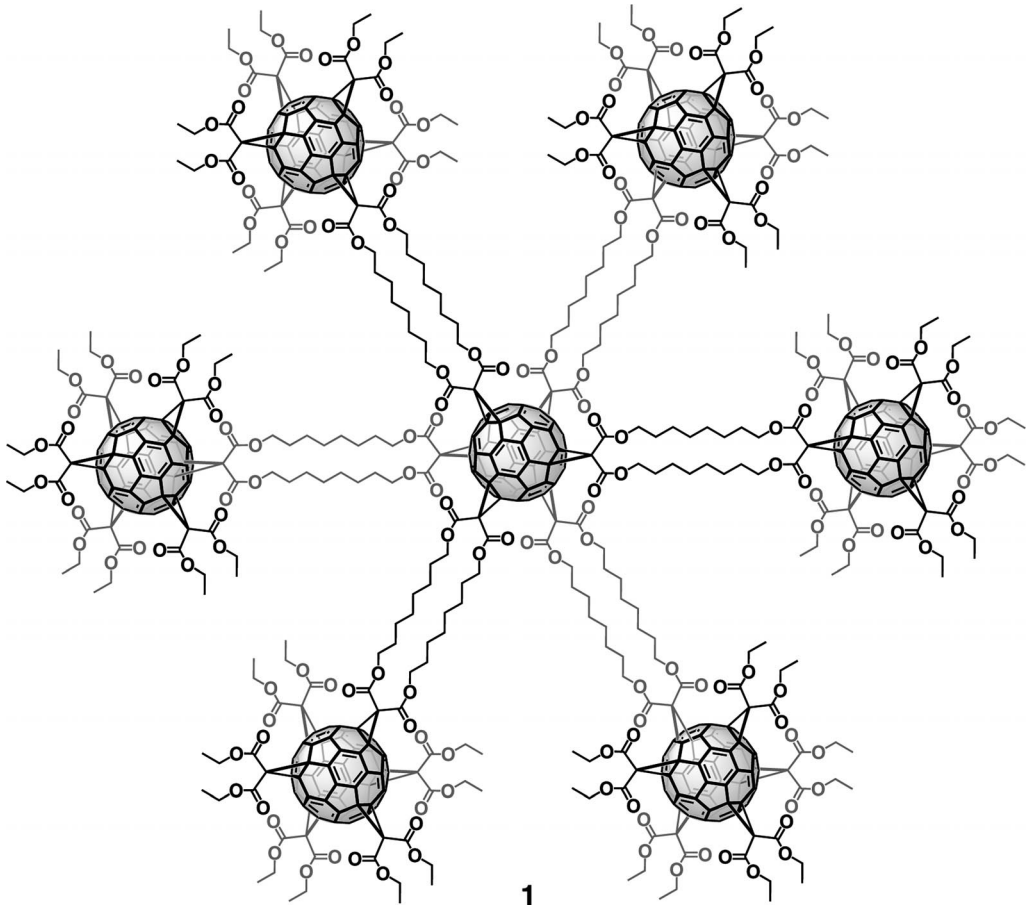

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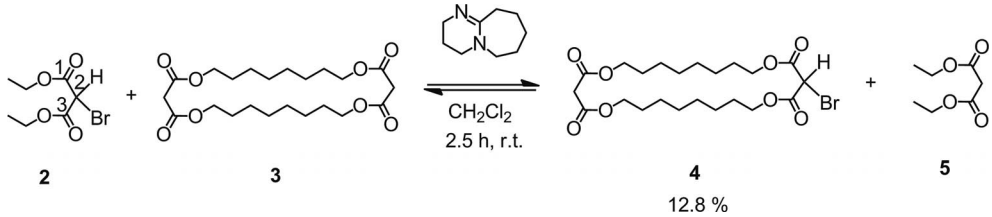
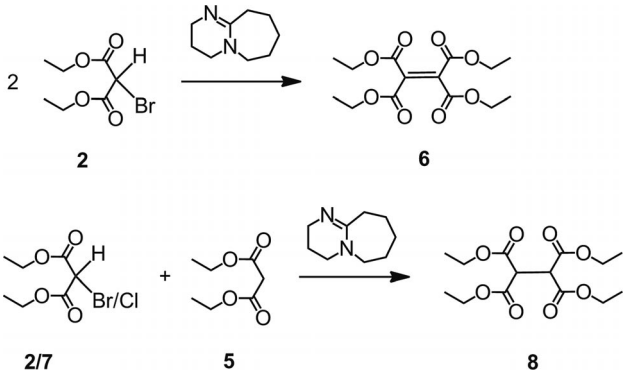
Figure 1. Intended heptafullerene target molecule **1** as proof of applicability.



Scheme 2. Observed bromine exchange reactions between **2** and **3**.

We observed the formation of the monobrominated cyclo-[2]-octylmalonate **4** and diethyl malonate **5**, which are in equilibrium with the starting material. Clearly, Br exchange reactions take place. Interestingly, the exclusive treatment of **2** with DBU led to the formation of tetraethyltetracarboxyethene (**6**, Scheme 3). As a consequence, bromomalonates are indeed not suitable for a selective step-by-step functionalization sequence of oligomalonates, as these side reactions will also occur in the presence of C_{60} under the usual cyclopropanation reaction conditions.

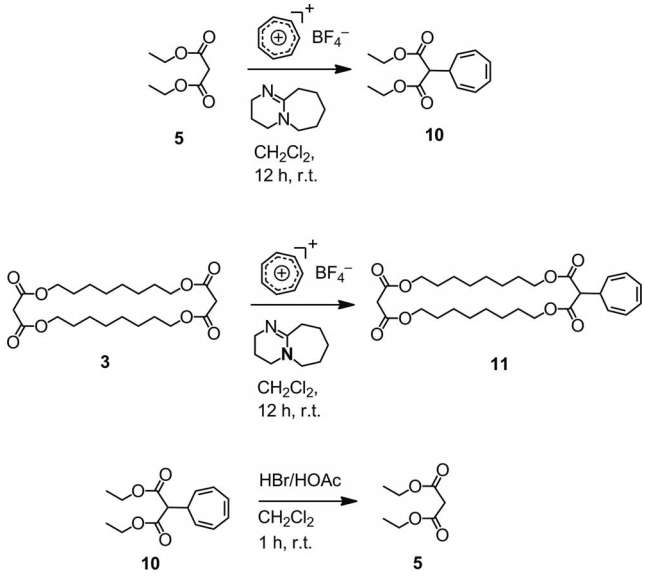


Scheme 3. Observed side reactions during the treatment of bromo- and chloromalonates **2** and **7** with DBU.

It is reasonable to assume that these side reactions involve nucleophilic substitutions at the bromine atoms attached to C2 atoms of the malonate. The corresponding nucleophiles are the malonate anions formed after deprotonation with DBU. Nucleophilic substitution of bromine atoms is a common phenomenon.[2,8,9,10] As nucleophilic substitutions of chlorine atoms are much more difficult,[8] we then investigated whether there is also scrambling if chloro- instead of bromomalonates are used. In the analogous control experiment as that depicted in Scheme 2 but with diethyl 2-chloromalonate (**7**) instead of its brominated counterpart, we observed no Cl exchange. This positive result suggested that monochlorinated oligomalonates should be able to undergo selective monofullerenylation. However, first we had to test whether cyclopropanation of C_{60} with chloromalonates is possible at all. Although chloromalonates have been used for S_N2' reactions on fullerenes,[11] no nucleophilic cyclopropanation reactions have been described. The test reaction we employed was performed with **7** and DBU as base (Scheme 4).

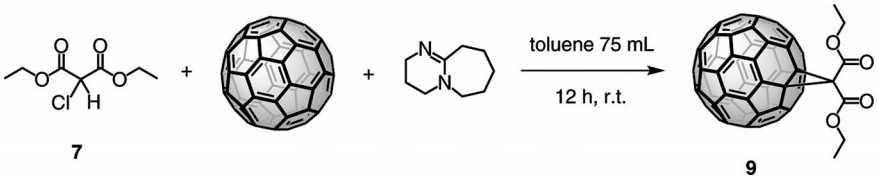
The targeted monoadduct **9** was formed and, hence, chloromalonates can be used as precursor addends for the nucleophilic cyclopropanations of fullerenes. The isolated yield of 15%, however, is lower than that of the corresponding reaction of C_{60} with diethyl-2-bromomalonate, in which **9** was obtained in 45% yield.[2]

As an alternative approach would have been to find a protecting group for the malonates, we examined whether the tropylium cation was suitable as a protecting group (Scheme 5) that would allow access to oligomeric malonates with just one binding site for nucleophilic cyclopropanation. The reaction of tropylium tetrafluoroborate with a malonic ester successfully yields the malonates **10** and **11**, in which one C–H-acidic hydrogen is substituted by the tropylium ion. Deprotection of **10** with HBr (48% in acetic acid), diluted in dichloromethane, was achieved in one hour. As expected, the protected diethylmalonate **10** did not undergo a nucleophilic cyclopropanation reaction with C_{60}. However, if unprotected malonates were present, the cycloheptatriene group decomposed to unidentified compounds, which showed ^{1}H NMR signals in the aromatic region, so this method was unsuitable for this purpose.

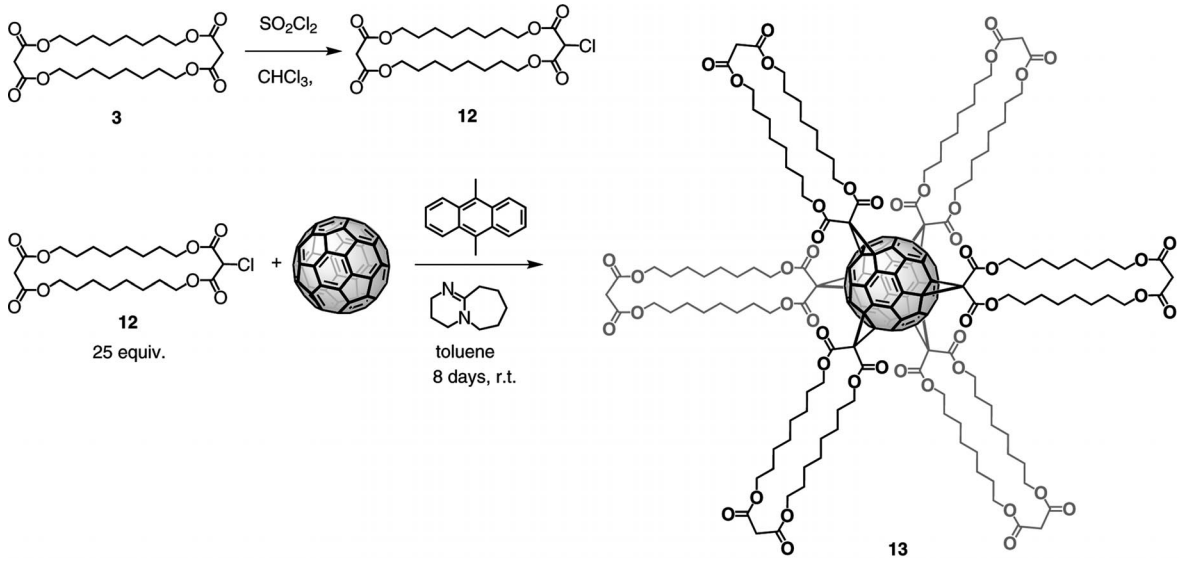


Scheme 5. Formation of the tropylium derivative **11** and deprotection of the tropylium derivative **10**.

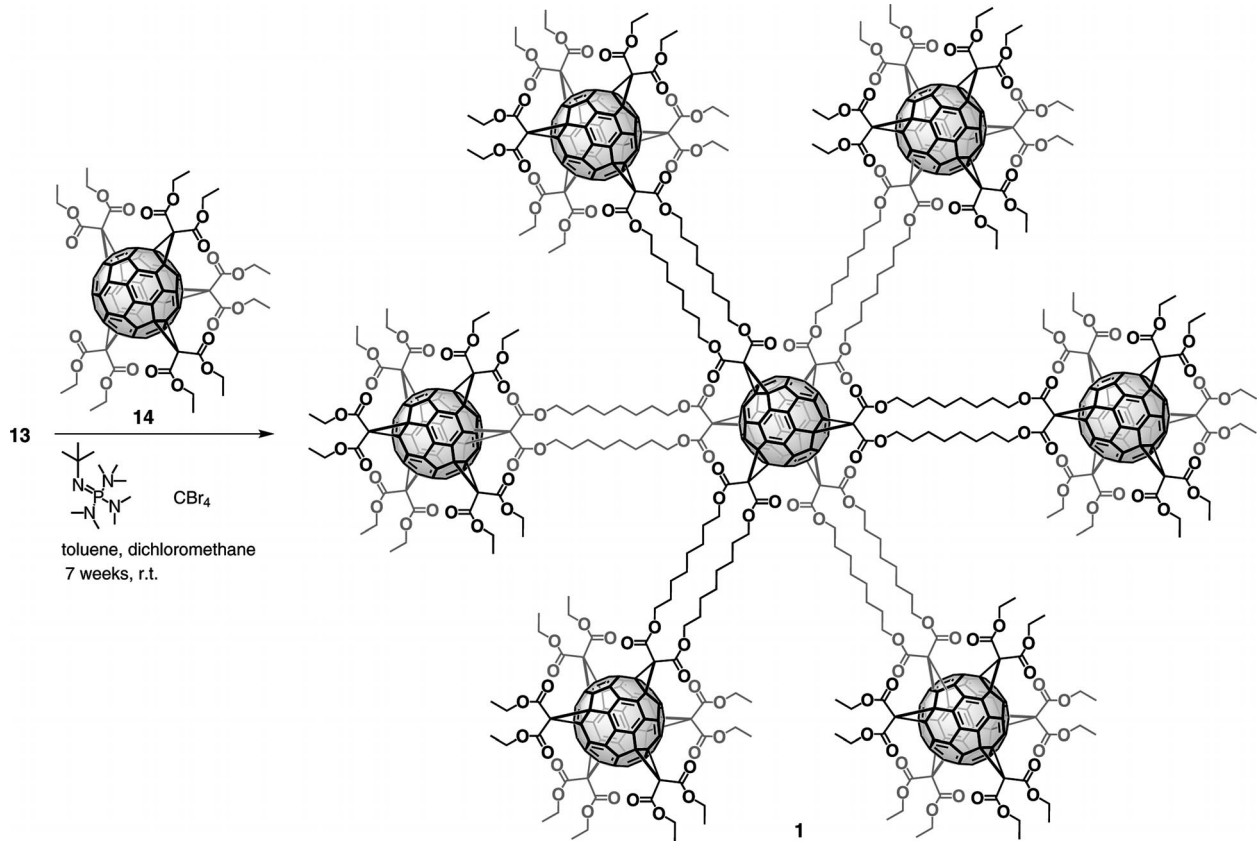
Thus, we relied on the preactivation of the malonates with chlorine atoms. For proof of principle, we investigated the sequential synthesis of the heptafullerene **1**, which is similar to one that we synthesized recently by following a less efficient route.[12] In our old pathway, fullerene-containing addends were added to a blank center. The necessary templating significantly impeded the reaction, and additions at the wrong positions made the use of HPLC necessary to remove side-products. In contrast, in our new ap-



Scheme 4. Cyclopropanation of C_{60} with **7**.



Scheme 6. Synthesis of the hexakis-adduct **13**.



Scheme 7. Divergent synthesis of the heptafullerene **1**.

proach depicted in Schemes 6 and 7, the octahedral addition pattern of the central fullerene core is completed before the terminal fullerenes are connected in the final step. For this purpose, we first had to synthesize the monochlorinated cyclo-[2]-octylmalonate **12** (Scheme 6), which was accomplished by heating **3** to reflux in the presence of a stoichiometric amount of sulfuryl dichloride for 12 h. The amount of chloroform solvent was kept as low as possible. To separate the product from the starting material, column chromatography of the crude product in dichloromethane was performed. Efficient separation required the use of relatively dilute solutions of the product mixtures. A large amount of starting material could be recovered. Subsequently, a 25-fold excess of addend **12** was allowed to re-

act with C_{60} by templating with 9,10-dimethylanthracene (DMA).[13] The highest yields (3.3%) of the T_h-symmetric hexakis-adduct **13** were obtained with toluene as solvent and DBU as a base. Purification was performed by column chromatography on 15 micron silica with toluene/ethyl acetate (4:1) as eluent. The expected hexakisaddition was confirmed by mass spectrometry. In the ^{13}C NMR spectrum, the T_h-symmetric addition pattern was obvious by the matching number of signals for the depicted symmetry, especially the two characteristic signals for the sp^2 C atoms of the fullerene core at δ = 145.8 and 141.0 ppm[14] and the two carbonyl signals at δ =166.48 and 163.84 ppm.[14]

The final step was the conversion of the hexakis-adduct **13** to the target molecule **1** (Scheme 7) with the terminating building blocks **14**. Compound **14** represents a [5.0]-pentakis-adduct of C_{60}, for which we recently disclosed an efficient access based on the photocleavage of one reversibly binding addend of the corresponding [5:1]-isoxazoline precursor.[15,16] The coupling of **14** to **13** was performed in toluene by the stoichiometric addition of **13**, tetrabromomethane, *tert*-butylimino-tri(pyrrolidino)phosphorane (P_1-*t*Bu),[17] and a slight excess of addend **14**. Although both fullerene-containing components readily precipitate under these conditions, the reaction was left for one month. Subsequently, dichloromethane was added to redissolve the reagents. The addition of an excess of tetrabromomethane, phosphazene base, and some amount of the addend **14** in three portions over one month gave the seven-membered fullerene adduct **1** in 43% isolated yield.

The straightforward workup of the reaction mixture and the purification of **1** was accomplished by plug filtration. For this purpose, the plug was packed with a toluene/ethyl acetate mixture (6:1), and the free pentakis-adduct was eluted. Subsequently, the product was eluted with a toluene/ethyl acetate (2:1) mixture. Distinct product signals were observed in both ESI (four charges) and MALDI (one charge) MS, but no signals for incompletely reacted starting materials were observed. The characteristic sp^2 C_{60} ^{13}C NMR signals[14] were found at δ = 145.8, 145.7, 141.0, 141.1 ppm. The absence of unidentified signals in the regions around δ = 45 and slightly less than 30 ppm, which would be characteristic of unattached malonates, corroborates the complete substitution. Thus, we can conclude that, as incompletely substituted molecules such as penta- or hexafullerenes would have been difficult to separate owing to their similar polarity and solubility, the conversion to **1** was exhaustive and no such lower clusters exist in the reaction mixture. The UV/Vis spectrum of the product shows a pattern characteristic of hexakis-adducts, especially the absorptions at 316 and 334 nm,[14] which is further evidence that the fullerenes are attached in a symmetric pattern.

Conclusions

We have developed a concept for the sequential fullerenylation of bis-malonates with different fullerenes. This approach relies on the finding that a) chloromalonates can be used for the nucleophilic cyclopropanation of [6,6] double bonds of C_{60} and b) chloromalonates, in contrast to bromomalonates, do not undergo base-catalyzed halogen-exchange reactions. For the proof of concept, we synthesized the heptafullerene **1** by using a divergent approach based on the hexakis-adduct **13** with six bis-malonate addends in octahedral positions, each of which is suitable for an additional cyclopropanation of a fullerene building block. The method for the sequential and orthogonal oligofunctionalization of oligomalonates bears many possibilities for the design of highly functional oligofullerene architectures with tunable properties. The systematic exploration of these opportunities is currently underway in our laboratories.

Experimental Section

General Remarks and Chemicals: Chemicals were purchased from commercial sources and were used without further purification (unless otherwise stated). C_{60} was purchased from IoLiTec Nanomaterials. Solvents were distilled before use; solvents that generated acid had K_2CO_3 in the distillation flask. For reactions with fullerenes, HPLC grade solvents were used. The dichloromethane used for the synthesis of **3** was dried by distillation from lithium aluminum hydride. TLC: Merck TLC silica gel 60 F_{254}, $KMnO_4$ (1% solution in 1% aqueous KOH) was used to develop the plates. Flash chromatography: Interchim puriFlash 430 instrument, SIHC-JP 15 μm 40 g column, substances purified portionwise. UV/Vis spectroscopy: Varian Cary 5000 spectrophotometer, CH_2Cl_2 solvent, absorption maxima given in nm, extinction coefficients given in $M^{-1}cm^{-1}$. IR spectroscopy: attenuated total reflectance (ATR), Bruker FTIR Tensor 27 instrument. Abbreviations: w weak, m medium, s strong. NMR spectroscopy: Bruker Avance 400 or Avance 300 spectrometer. Field strengths are given as the resonance frequency of the respective nucleus. The chemical shifts are given in ppm relative to tetramethylsilane (TMS). Abbreviations: s singlet, d doublet, t triplet, q quartet, m multiplet, br. broad. Spectra were recorded at room temperature. MALDI MS: Shimadzu Axima Confidence instrument (TOF). ESI MS: Bruker Daltronics micrOTOF (TOF) instrument. Matrices: (*E*)-2-(3-(4-(*tert*-butyl)-phenyl)-2-methylallylidene)malononitrile (dctb), 3,5-dimethoxy-4-hydroxycinnamic acid (sin).

Cyclo-[2]-octylmalonate (3): The procedure in ref.[5] was improved as follows: 1,8-octanediol (8 g, 54.7 mmol, 1 equiv.) and pyridine (8.66 g, 8.81 mL, 54.7 mmol, 1 equiv.) were dissolved in anhydrous dichloromethane (4 L), and malonyl dichloride (7.71 g, 5.32 mL, 54.7 mmol, 1.3 equiv.) was dissolved in dry dichloromethane and added portionwise over 4 d. The solution was stirred for 2 d and then concentrated to 600 mL. Ethyl acetate (67 mL) was added, and the mixture was plug-filtered through silica (6 × 12 cm plug). The solvent was removed, and the mixture was chromatographically purified (SiO_2, dichloromethane/ethyl acetate, 19:1, diluted, at least 1.5 L bed volume), yield up to 2.7 g (23%). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.11 (t, $^3J_{H,H}$ = 6.7 Hz, 8 H, CH_2O), 3.33 (s, 4 H, $COOCH_2COO$), 1.60 (m, 4 H, CH_2CH_2O), 1.3 (m, 16 H, $CH_2CH_2CH_2CH_2O$) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 166.4 (4 C, *C*=O), 65.4 (4 C, CH_2O), 42.1 ($COOCH_2COO$), 29.2 (4 C, CH_2CH_2O), 28.4 [4 C, $CH_2(CH_2)_2O$], 25.8 [4 C, $C(CH_2)_3O$] ppm. IR (ATR, diamond): $\tilde{\nu}$ = 2960 (w), 2922 (m), 2855 (m), 1740 (s), 1478, 1389, 1326 (s), 1254 (s), 1217 (s), 1138 (s), 1064 (w), 1028 (m), 1003 (m), 892 (m), 724 (m) cm^{-1}. MS (MALDI, dhb): *m*/*z* = 429 $[M + H]^+$, 451 $[M + Na]^+$. $C_{22}H_{36}$ (300.53): calcd. C 61.66, H 8.47; found C 60.93, H 8.35.

Cation Exchange Experiment Resulting in Bis-malonate 4 and Diethyl Malonate 5: Diethyl bromomalonate (47.573 mg, 33.9 μL, 0.199 mmol, 1 equiv.) and cyclo-[2]-octylmalonate (**2**, 85 mg, 0.199 mmol, 1 equiv.) were dissolved in toluene (5 mL). DBU (30.3 mg, 29.7 mL, 0.199 mmol, 1 equiv.) was added, and the mixture was stirred for 2.5 h. Acetic acid (100 μL) was added, and the resulting solution was purified by column chromatography (SiO_2, dichloromethane), yield 13 mg, 12.8%. Brominated malonate **4**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.83 (s, 1 H, C*H*Br), 4.35–4.08 (m, 8 H, CH_2O), 3.34 [s, 2 H, C*H*(C=O)$_2$], 1.6 (m, 8 H, CH_2CH$_2$O), 1.3 (m, 16 H, CH_2CH_2CH$_2$CH$_2$O) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 166.5 [2 C, CH$_2$(*C*=O)$_2$], 164.5 [2 C, CHBr(*C*=O)$_2$], 67.2, 65.5 (4 C, *C*H$_2$O), 43.2 (1 C, *C*HBr), 42.2 [1 C, *C*H$_2$(C=O)$_2$], 29.3, 29.2 [4 C, *C*H$_2$CH$_2$O], 28.5, 28.4 (4 C, *C*H$_2$CH$_2$CH$_2$O), 25.8, 25.7 (4 C, *C*H$_2$CH$_2$CH$_2$CH$_2$O) ppm. Data for diethyl malonate **5**: ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 166.6, 61.5, 41.7, 14.0 ppm.

Cation Exchange Experiment Resulting in Bis-malonate 4 and Compound 6: Diethyl bromomalonate (476 mg, 339 μL, 1.99 mmol, 10 equiv.), diethyl malonate (**5**, 319 mg, 302 μL, 1.99 mmol, 1 equiv.), and cyclo-[2]-octylmalonate (**3**, 85 mg, 0.199 mmol, 1 equiv.) were dissolved in toluene (5 mL). DBU (303 mg, 297 mL, 1.99 mmol, 10 equiv.) was added, and the mixture was stirred for 12 h. Acetic acid (0.5 mL) was added, and the resulting solution was plug-filtered twice (SiO_2, dichloromethane/ethyl acetate, 1:1 and then SiO_2, dichloromethane, 6 bed volumes dichloromethane/ethyl acetate, 1:1). The resultant product was purified by column chromatography (dichloromethane/ethyl acetate, 19:1). In the fraction with R_f = 0.11 in dichloromethane, 18 mg of the monobrominated cyclic compound was obtained. Furthermore, tetraethyltetracarboxyethene (**6**, at least 60 mg) and tetraethyl 1,1,2,2-ethanetetracarboxylate were also found. Data for brominated malonate **4**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.83 (s, 1 H, C*H*Br), 4.35.4.08 (m, 8 H, CH_2O), 3.34 [s, 2 H, C*H*(C=O)$_2$], 1.6 (m, 8 H, CH_2CH$_2$O), 1.3 (m, 16 H, CH_2CH_2CH$_2$CH$_2$O) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 166.5 [2 C, CH$_2$(*C*=O)$_2$], 164.5 [2 C, CHBr(*C*=O)$_2$], 67.2, 65.5 (4 C, *C*H$_2$O), 43.2 (1 C, *C*HBr), 42.2 [1 C, *C*H$_2$(C=O)$_2$], 29.3, 29.2 (4 C, *C*H$_2$CH$_2$O), 28.5, 28.4 (4 C, *C*H$_2$CH$_2$CH$_2$O), 25.8, 25.7 (4 C, *C*H$_2$CH$_2$CH$_2$CH$_2$O) ppm. Data for **6**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.29 (q, $^3J_{H,H}$ = 7.2 Hz, 8 H, CH_2O), 1.29 (t, $^3J_{H,H}$ = 7.2 Hz, 12 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 162.3 (4 C, *C*=O), 135.3 (2 C, *C*=*C*), 62.6 (4 C, *C*H$_2$O), 13.8 (4 C, *C*H$_3$) ppm. Data for tetraethyl 1,1,2,2-ethanetetracarboxylate **8**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.24–4.12 (m, 8 H, CH_2O), 4.09 (s, 2 H, C*H*-C*H*), 1.24 (t, $^3J_{H,H}$ = 7 Hz, CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 167.0 (4 C, *C*=O), 62.0 (4 C, *C*H$_2$O), 51.4 [2 C, (C=O)$_2$*C*H*C*H(C=O)$_2$], 13.9 (4 C, *C*H$_3$) ppm. HRMS (ESI, CH_2Cl_2/MeCN/MeOH): calcd. for $C_{14}H_{23}O_8$ [M + H]$^+$ 319.13874; found 319.13946; calcd. for $C_{14}H_{22}NaO_8$ [M + Na]$^+$ 341.12069; found 341.12146;

Monoadduct 9: Diethyl chloromalonate (45.5 mg, 37.8 μL, 0.236 μmol, 1.13 equiv.) and C_{60} (170 mg, 236 μmol, 1.13 equiv.) were dissolved in toluene (75 mL). DBU (31.7 mg, 31.1 μL, 0.209 μmol, 1 equiv.) was added, and the mixture was stirred for 21 h. The mixture was plug-filtered (SiO_2, toluene) and purified by column chromatography (SiO_2, toluene). R_f = 0.726, yield 28 mg (15% based on DBU). Product **9** was verified by NMR spectroscopy and HRMS. HRMS (ESI, CH_2Cl_2/MeCN/toluene): calcd. for $C_{67}H_{10}O_4$ [M]$^+$ 878.05846; found 878.05829.

Tropylium-Protected Diethyl Malonate 10: Tropylium tetrafluoroborate (293 mg, 1.24 mmol, 1 equiv.) was suspended in dichloromethane (5 mL). Diethyl malonate **5** (200 mg, 210 μL, 1.24 mmol, 1 equiv.) and DBU (88.8 mg, 192 μL, 1.24 mmol, 1 equiv.) were added and the mixture was stirred for 12 h. The mixture was filtered and purified by column chromatography (SiO_2, CH_2Cl_2), yield 70% ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.68 (m, 2 H, CHCHCH=CHC*H*=C*H*), 6.24 (2 H, CHCHCH=C*H*), 5.36 (2 H, CHCHC*H*=CH), 4.21 (q, $^3J_{H,H}$ = 7 Hz, 4 H, CH_2O), 3.65 [d, $^3J_{H,H}$ = 10 Hz, 1 H, CHC*H*(C=O)$_2$], 2.73 [m, 1 H, C*H*CH(C=O)$_2$], 1.27 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 168.1 (2 C, *C*=O), 130.9 (2 C, CHCH*C*H=CH), 126.6 (2 C, CHCHCH=CH*C*H=*C*H), 122.3 (2 C, CHCHCH=*C*H), 61.4 (2 C, *C*H$_2$O), 52.7 [2 C, CH*C*H(C=O)$_2$], 38.25 [2 C, *C*HCH-(C=O)$_2$], 14.1 (2 C, *C*H$_3$) ppm. HRMS (ESI, CH_2Cl_2/MeCN/toluene): calcd. for $C_{14}H_{18}NaO_4$ [M + Na]$^+$ 273.10973; found 273.10998. IR (ATR, diamond): $\tilde{\nu}$ = 2983 (m), 2939 (w), 2906 (w), 1728 (s), 1464 (w), 1446 (w), 1369 (w), 1299 (m), 1258 (m), 1229 (m), 1151 (s), 1131 (w), 1096 (w), 1028 (s), 860 (m), 744 (w), 701 (s), 593 (m) cm^{-1}.

Tropylium-Protected Bismalonate 11: Tropylium hexafluorophosphate (138 mg, 0.583 mmol, 1 equiv.) was suspended in dichloromethane (4 mL). Cyclo-[2]-octylmalonate (**3**, 250 mg, 0.583 mmol, 1 equiv.) and DBU (88.8 mg, 87 μL, 1 equiv.) were added, and the mixture was stirred for 48 h. The mixture was purified by column chromatography (SiO_2, CH_2Cl_2), yield 37%. R_f (CH_2Cl_2) = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.64 (m, 2 H, CHCHCH=CHC*H*=C*H*), 6.23 (2 H, CHCHCH=C*H*), 5.26 (2 H, CHCHC*H*=CH) 4.18 (4 H, CHCHC=OOCH_2), 4.12 (4 H, CH$_2$C=OOCH_2), 4.02 (4 H, CHCHC=OOCH_2), 3.61 [d, 1 H, CHC*H*(C=O)$_2$], 3.34 [2 H, CH_2(C=O)$_2$] 2.7 (1 H, C*H*CH(C=O)$_2$), 1.61 (8 H, CH_2CH$_2$O), 1.29 (16 H, CH_2CH_2CH$_2$CH$_2$O) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = [ppm] = 168.1 (2 C, C=O), 166.4 (2 C, C=O), 130.9 (2 C, CHCH*C*H=CH) 125.6 (2 C, CHCHCH=CH*C*H=*C*H) 122.4 (2 C, CHCHCH=*C*H), 65.43, 65.36 (4 C, *C*O), 52.71 [(C=O)$_2$*C*HCH], 42.1 [(C=O)$_2$*C*H$_2$], 38.0 [(C=O)$_2$CH*C*H] 29.2 (OCH$_2$*C*H$_2$), 28.4 (OCH$_2$CH$_2$*C*H$_2$), 25.8 (OCH$_2$CH$_2$CH$_2$*C*H$_2$) ppm. MS (MALDI): *m*/*z* = 523 [M – 4H + Li]$^+$, 554 [M – 4H + K]$^+$. MS (MALDI, sin): *m*/*z* = 544 [M – 2H + Na]$^+$. HRMS (ESI, CH_2Cl_2/MeCN/MeOH): calcd. for $C_{29}H_{42}NaO_8$ [M + Na]$^+$ 541.2771; found 541.27851. IR (ATR, diamond): $\tilde{\nu}$ = 3022 (w), 2956 (w), 2927 (s), 2853 (m), 1740 (s), 1726 (s), 1476 (w), 1392 (w), 1321 (m), 1262 (m), 1215 (m), 1164 (m), 1137 (m), 1063 (w), 1026 (w), 999 (m), 977 (w), 734 (s), 698 (s) cm^{-1}.

Cleavage of Tropylium-Protected Diethyl Malonate 10: Tropylium-protected diethyl malonate **10** (50 mg, 0.2 mmol) was dissolved in anhydrous dichloromethane (10 mL). HBr (2 mL) was added, and the mixture was stirred for 1 h at room temperature. Water (10 mL) was added. The phases were separated, and the organic phase was stirred over $NaHCO_3$ (5 g). After filtration and removal of the solvent, diethyl malonate was obtained without traces of **10**, yield 39%.

Monochlorinated Bis-malonate 12: To cyclo-[2]-octylmalonate (**3**, 3.17 g, 7.40 mmol, 1 equiv.) suspended in chloroform (4.4 mL) was added sulfuryl dichloride (1 g, 0.5985 mL, 7.40 mmol, 1 equiv.), and the mixture was heated to 70 °C for 24 h. The resultant mixture was diluted with dichloromethane (200 mL) and chromatographically purified very slowly over a 200 mL bed-volume plug (SiO_2, CH_2Cl_2). Unreacted starting material can be recovered by washing the plug with dichloromethane/ethyl acetate, 1:1, yield 1.233 g (36%, 70% based on recovered starting material). R_f = 0.155 (product). Impurities: R_f = 0.352 (both sides monochlorinated), 0.2535 (one side dichlorinated). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.84 (1 H, C*H*Cl), 4.2 (2m, 4 H, CH_2OC=OCHCl), 4.12 (t, 4 H, CH_2O-C=OCH$_2$), 3.33 [s, 2 H, CH_2(C=O)$_2$], 1.63 (m, 8 H, CH_2CH$_2$O),

1.32 (16 H, $CH_2CH_2CH_2CH_2O$) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 166.4, 164.3 (4 C, *C*=O), 67.11, 65.4 (4 C, CH_2O), 55.8 (1 C, *C*HCl), 42.1 [1 C, C(C=O)CH_2], 29.21, 29.18 (4 C, CH_2CH_2O), 28.4, 28.3 (4 C, $CH_2CH_2CH_2O$), 25.8, 25.7 (4 C, $CH_2CH_2CH_2CH_2O$) ppm. HRMS (ESI, MeCN/MeOH): calcd. for $C_{22}H_{35}ClNaO_8$ $[M + Na]^+$ 485.19127; found 485.19089. IR (ATR, diamond): $\tilde{\nu}$ = 2935 (s), 2856 (m), 1735 (s), 1469 (m), 1318 (s), 1306 (s), 1282 (s), 1202 (m), 1164 (m), 1147 (m), 1000 (m) cm^{-1}.

Hexakis-adduct 13: Malonate **12** (400 mg, 864 umol, 25 equiv.), 9,10-dimethylanthracene (70 mg, 414 umol, 12 equiv.), and C_{60} (24 mg, 34.6 umol, 1 equiv.) were dissolved in toluene (12 mL) and stirred for 3 h. DBU (63.1 mg, 62.0 µL, 414 umol, 12 equiv.) was added, and the mixture was stirred for 5 d. Further DBU (15.8 mg, 15.5 µL, 104 umol, 3 equiv.) was added, and the mixture was stirred for an additional 3 d. Ethyl acetate (4 mL) was added, and the mixture was plug-filtered (SiO_2, toluene/ethyl acetate, 4:1). The solvent was removed, and the crude mixture was purified twice by flash chromatography (SiO_2, toluene/ethyl acetate, 4:1; the second time on 15 µ grain size SiO_2 and very slowly), yield 16 mg, (13.7% based on fullerene, 3.3% based on malonate). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.22 (24 H, $C_{60}C$=OOCH_2), 4.13 (24 H, CH_2=OOCH_2), 3.4 [12 H, CH_2(C=O)$_2$], 1.75–1.6 (48 H, CH_2CH_2O), 1.567 (128 H, $CH_2CH_2CH_2CH_2CH_2$) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 166.5 [12 C, CH_2(*C*=O)$_2$], 163.8 [12 C, C_{60}=C(*C*=O)$_2$], 145.8, 141.0 (48 C, C_{60} sp^2), 69.1 (12 C, C_{60} sp^3), 67.0 (12 C, C_{60}=CC=OO*C*H$_2$), 65.6 (12 C, H_2CC=OO*C*H$_2$), 45.3 [6 C, C_{60}=*C*(C=O)$_2$], 42.3 [6 C, H_2C(C=O)$_2$], 29.4 (24 C, CH_2CH_2O), 28.6, 28.5 (24 C, $CH_2CH_2CH_2O$), 25.9 (24 C, $CH_2CH_2CH_2CH_2O$) ppm. MS (MALDI, sin): *m*/*z* = 3302 $[M + Na]^+$, 3303 $[M + Na]^+$, 3304 $[M + 2H + Na]^+$, 3305 $[M + 3H + Na]^+$, 3305 $[M + 4H + Na]^+$. HRMS (ESI, MeCN/MeOH): calcd. for $C_{192}H_{204}Na_2O_{48}$ $[M + 2H + 2Na]^{2+}$ 1662.67328; found 1662.67012. IR (ATR, diamond): $\tilde{\nu}$ = 2929 (s), 2856 (m), 1732 (s), 1465 (w), 1387 (w), 1260 (m), 1212 (s), 1158 (w), 1081 (w), 1019 (m), 802 (m), 715 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) 245 (87000), 271 (66000), 282 (71000), 317 (45000), 335 (36000), 381 (5000) nm.

Heptafullerene 1: Hexakis-adduct **13** (31 mg, 9.452 mmol, 1 equiv.) was dissolved in toluene (3 mL). A solution of pentakis-adduct **14** (114 mg, 75.618 mmol, 8 equiv.) in toluene (5 mL) was added. The starting materials precipitated. Solutions of CBr_4 (18.8 mg, 56.7 mmol, 6 equiv.) and P_1-*t*Bu (13.3 mg, 14.4 µL, 56.7 mmol, 6 equiv.) were added, and the mixture was stirred for 22 d. Dichloromethane was added until the precipitate dissolved, and further pentakis-adduct **14** (21 mg, 14 mmol, 1.5 equiv.), CBr_4 (31 mg, 94.5 mmol, 10 equiv.), and P_1-*t*Bu (22.2 mg, 24 µL, 94.5 mmol, 10 equiv.) were added portionwise over 2 weeks, and the mixture was stirred for another 2 weeks. Ethyl acetate (5 mL) was added, and the mixture was plug-filtered (SiO_2, toluene/ethyl acetate, 4:1). The solvent was evaporated, and the mixture was purified by column chromatography (SiO_2, toluene/ethyl acetate, 6:1; toluene/ethyl acetate, 2:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.30 (q, $^3J_{H,H}$ = 7.0 Hz, 120 H, CH_3CH_2O), 4.22 (m, 48 H, CH_2CH_2O), 1.70 ppm (48 H, CH_2CH_2O), 1.36 ppm (96 H, $CH_2CH_2CH_2CH_2O$), 1.30 ppm (t, $^3J_{H,H}$ = 7.0 Hz, 180 H, CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 163.81, 163.78, 163.75 (84 C, C=O), 145.8, 145.7, 141.1, 141.0 (336 C, C_{60} sp^2), 69.09, 69.05, 69.01, 67.0 (84 C, C_{60} sp^3), 62.8 (84 C, H_2CO), 45.31,45.29, 45.27, 45.24 [42 C, *C*(C=O)$_2$], 29.46, (24 C, $CH_2CH_2CH_2O$), 28.48, (24 C, $CH_2CH_2CH_2O$), 26.0, (24 C, $CH_2CH_2CH_2CH_2O$) 14.0 (60 C, CH_3) ppm. MS (MALDI, dctb): *m*/*z* = 12330 $[M - 2H]^+$. HRMS (ESI, CH_3CN/MeOH/ HCOOH): calcd. for $C_{758}{}^{13}C_8H_{492}Na_4O_{168}$ $[M + 4Na]^{4+}$ 3106.74488 found; 3106.75364. IR (ATR, diamond): $\tilde{\nu}$ = 2980 (m), 2934 (m), 2857 (m), 1742 (s), 1464 (w), 1368 (w), 1262 (s), 1216 (s), 1079 (m), 1043 (m), 1018 (m), 857 (w), 715 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 246 (418000), 274 (415000), 282 (403000), 316 (333000), 334 (290000), 380 (71000) nm.

Supporting Information (see footnote on the first page of this article): NMR spectra of compounds **1**, **4**, **10**, **11**, **12**, **13**, ESI-MS, MALDI MS and UV/Vis data of **1**.

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